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(54) **Thermoplastic compositions containing polyphenylene ether resin**

Thermoplastische Zusammensetzung, die Polyphenylenetherharn enthält

Composition thermoplastique contenant des résines polyéther de phénylène

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<b>EP-A- 0 176 060</b>	<b>EP-A- 0 297 633</b>
<b>EP-A- 0 372 321</b>	<b>EP-A- 0 467 113</b>
<b>EP-A- 0 469 799</b>	<b>EP-A- 0 520 146</b>
<b>US-A- 4 277 575</b>	<b>US-A- 5 104 937</b>

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**EP 0 639 620 B1**

**Description**

**[0001]** This invention generally relates to thermoplastic compositions containing polyphenylene ether resin and elastomeric multiblock copolymers, and more particularly, to a blend of multiblock polymers, and to articles made therefrom.

**[0002]** Polyphenylene ether resin (also known and hereinafter referred to as "PPE") has become widely accepted in the plastics industry because of its desirable physical and chemical properties, such as high heat resistance and dimensional stability. PPE by itself is dielectric and also somewhat flame-retarding. Such benefits promote its use in certain products, for example, as an insulating material for electrical wire.

**[0003]** PPE-based compositions for these insulating applications sometimes include polyolefins, and exhibit improved impact strength and chemical resistance. Reference is therefore made here to U.S. -A-5 166 264, filed June 23, 1989 (G. Lee, Jr., and J. Yates III), and EP-A-0413972 both of which are assigned to the assignee of the present application.

**[0004]** However, the inclusion of olefinic components can decrease the flame retardance of the overall composition, thereby necessitating the addition of special additives to regain this important property. As an illustration, U.S. -A-4,808,647 (V. Abolins et.al.) describes the use of a multi-component flame retardant composition which includes an organic phosphate and a brominated material such as a tetrabromobisphenol-A oligomeric polycarbonate.

**[0005]** While the compositions described in the Abolins patent exhibit excellent properties suitable for many applications, it is often desirable to minimize or eliminate the use of bromine or other halogen-containing additives in compositions designed for certain products. For example, the wire insulation compositions mentioned above frequently cannot contain halogen additives because they could form corrosive compounds when exposed to high temperatures, thereby resulting in considerable damage to surrounding electrical equipment. Nevertheless, any modification of such an insulation composition must not result in significant decreases in the other important properties necessary for very durable products, e.g. flexibility and "stretchability" (elongation).

**[0006]** In co-pending U.S. -A- 5294655 filed May 15, 1992 there are disclosed combinations of PPE resins with certain elastomeric multiblock copolymers and other additives such as siloxane fluids, poly-olefins, flame retardants, stabilizers, fillers and reinforcing agents. These compositions as reported therein have improved flexibility and elongation.

**[0007]** EP-A-0467113 discloses compositions having improved flexibility and elongation comprising PPE and a hydrogenated block copolymer having the structure A-B-A' where A and A' are polymerized vinyl aromatic hydrocarbon blocks and B is an ethylene-butylene block.

**[0008]** It is therefore apparent that a need still exists for polyphenylene ether-based compositions that provide even further improved flexibility, elongation and non-corrosive properties, as well as having flame retardant properties. In particular, a need exists for wire insulation compositions which are flame retardant, and which exhibit improved tensile elongation and improved flexibility over current wire coating compositions, while being halogen-free with respect to the flame retardant additive.

**SUMMARY OF THE INVENTION**

**[0009]** The present invention provides A flexible thermoplastic resin composition comprising in admixture a polyphenylene ether resin, from 10% by weight to 50% by weight of an elastomeric block copolymer based on the total weight of polyphenylene ether resin and elastomeric block copolymer from 1 to 30% by weight of a polyolefin based on the total weight of the composition, and from 1 to 25% by weight of a flame retardant plasticizer based on the total weight of the composition, said flame retardant plasticizer being a phosphate compound, characterized in that the elastomeric block copolymer comprises in admixture from 75% by weight to 25% by weight of a triblock copolymer having a hydrogenated structure of A-B-A' and correspondingly from 25% by weight to 75% by weight of a diblock copolymer having a hydrogenated structure of A-B, wherein A and A' are independently selected from polymerized vinyl aromatic hydrocarbon blocks and B is independently selected from an ethylene-alkylene block.

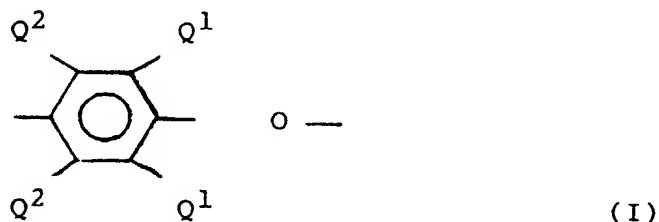
**[0010]** As also described below, the particular combination of PPE resin with these specific elastomeric block copolymer blends, i.e. blends of triblock and diblock, has surprisingly resulted in compositions which exhibit important properties which are dramatically superior to those in PPE compositions which contain only a triblock elastomeric copolymer.

**[0011]** Another embodiment of the present invention is an improved electrical conductor article which includes a very durable and flexible coating material formed from PPE resin and the blend of elastomeric block copolymers described herein. The coating material may be applied over the surface of the conductor, or may be used as a jacket layer applied over another wire insulating material.

**[0012]** Yet another embodiment of the present invention is an improved molded article having improved flexibility and improved elongation, as well as flame retardancy, particularly where such properties are wanted for molded articles.

## DETAILED DESCRIPTION OF THE INVENTION

[0013] Polyphenylene ether (PPE) is a well known class of synthetic polymeric resins as are methods of their preparation. Representative of polyphenylene ethers are those which comprise a plurality of recurring chain structural units having the formula:



wherein each  $Q^1$  is independently halogen, primary or secondary lower alkyl, phenyl, haloalkyl, aminoalkyl, hydrocarboxy, or halohydrocarboxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each  $Q^2$  is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarboxy or halohydrocarboxy as defined for  $Q^1$ .

[0014] The term "halogen" as used herein means chlorine, bromine, fluorine, or iodine.

[0015] Examples of primary lower alkyl groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-, 3- or 4-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-, 3-, 4-methylpentyl, and the corresponding heptyl groups. Examples of secondary lower alkyl groups are isopropyl, sec-butyl and 3-pentyl. Preferably, any alkyl radicals are straight chain, rather than branched. Most often, each  $Q^1$  is alkyl or phenyl, especially  $C_{1-4}$  alkyl, and each  $Q^2$  is hydrogen.

[0016] Both homopolymer and copolymer polyphenylene ethers are included. Representative homopolymers are those containing, for example, 2,6-dimethyl-1, 4-phenylene ether units. Representative copolymers include random copolymers containing such units in combination with (for example) 2,3,6-trimethyl-1, 4-phenylene ether units. Many suitable random copolymers, as well as homopolymers, are disclosed in the patent literature, see for example Hay, U. S.-A-3,306,874; US-A-3,306,875 and US-A-3,432,469, Geln Staaloff, U.S.-A-3,257,357 and US-A-3,257,358; Van Dort, U.S.-A-3,365,422, Bennett and Cooper, U.S.-A-3,639,656 US-A-3,642,699, US-A-3,733,299, US-A-3,838,102, US-A-3,661,848, and US-A-4,092,294; Olander, U.S.-A-4,083,838; White et.al. U.S.-A-4,806,602; and Brown et.al. U.S.-A-4,806,297.

[0017] Also included for use in the compositions of the invention are polyphenylene ethers containing moieties which modify properties such as molecular weight, melt viscosity and/or impact strength. Such polymers are described in the patent literature and may be prepared by grafting onto the polyphenylene ether in known manner such vinyl monomers as acrylonitrile and vinylaromatic compounds (e.g., styrene), or such polymers as polystyrenes and like polymers. The product may contain both grafted and ungrafted moieties. Other suitable polymers are the coupled polyphenylene ethers in which the coupling agent is reacted in known manner with the hydroxy groups of two polyphenylene ether chains to produce a higher molecular weight polymer containing the reaction product of the hydroxy groups and the coupling agent, provided substantial proportions of free hydroxy groups remain present. Illustrative coupling agents are low molecular weight polycarbonates, quinones, heterocycles, and formals.

[0018] The polyphenylene ether advantageously has a number average molecular weight ( $M_n$ ) within the range of 3,000-40,000 and a weight average molecular weight ( $M_w$ ) within the range of 20,000-80,000, as determined by gel permeation chromatography. Their intrinsic viscosity is most often in the range of 0.15-0.6 dl./g., as measured in chloroform at 25°C.

[0019] The polyphenylene ethers are typically prepared by the oxidative coupling of at least one corresponding monohydroxyaromatic compound. Particularly useful and readily available monohydroxyaromatic compounds are 2,6-xlenol (wherein each  $Q^1$  is methyl and each  $Q^2$  is hydrogen), whereupon the polymer may be characterized as a poly (2,6-dimethyl-1,4-phenylene ether), and 2,3,6-trimethylphenol (wherein each  $Q^1$  and one  $Q^2$  is methyl and the other  $Q^2$  is hydrogen).

[0020] A variety of catalyst systems are known for the preparation of polyphenylene ethers by oxidative coupling. There is no particular limitation as to catalyst choice and any of the known catalysts can be used. For the most part, they contain at least one heavy metal compound such as a copper, manganese or cobalt compound, usually in combination with various other materials.

[0021] A first class of preferred catalyst systems consists of those containing a copper compound. Such catalysts are disclosed, for example, in U.S.-A-3,306,874, US-A-3,306,875, US-A-3,914,266, and US-A-4,028,341.

[0022] They are usually combinations of cuprous or cupric ions, halide (i.e., chloride, bromide or iodide) ions and at

least one amine.

**[0023]** Catalyst systems containing manganese compounds constitute a second preferred class. They are generally alkaline systems in which divalent manganese is combined with such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one or more complexing and/or chelating agents such as dialkylamines, alkanolamines, alkylenediamines, o-hydroxyaromatic aldehydes, o-hydroxyazo compounds, W-hydroxoximes (monomeric and polymeric), o-hydroxyaryl oximes and B-diketones. Also useful are known cobalt-containing catalyst systems. Suitable manganese and cobalt-containing catalyst systems for polyphenylene ether preparation are well known in the art.

**[0024]** As another example, coupled PPE polymers may also be used in which the coupling agent is reacted with the hydroxy groups of two PPE chains to produce a higher molecular weight polymer.

**[0025]** It will be apparent to those skilled in the art from the foregoing that the polyphenylene ethers contemplated for use in the compositions of the present invention include all those presently known, irrespective of variations in structural units or ancillary chemical features.

**[0026]** In some embodiments, a polystyrene homopolymer or random copolymer resin may be included in the composition. These materials, which are very compatible with the PPE polymer, are known in the art and described, for example, in U.S.-A-3,383,435; US-A-4,189,411; and US-A-4,242,363. Illustrative resins of this type are polystyrene, poly-alpha-methyl styrene, poly-paramethyl styrene, polychlorostyrene, brominated polymers (e.g., those formed from dibromostyrene monomer), as well as styrene polymers modified by admixture or interpolymerization with natural or synthetic elastomeric materials, e.g., polybutadiene, polyisoprene, butyl rubber, EPDM rubber, and the like. Also contemplated are styrene-acrylonitrile copolymers (SAN), acrylate-styrene-acrylonitrile terpolymers (ASA), and styrene-acrylonitrile-butadiene terpolymers (ABS). Special mention is made of rubber-modified styrene polymers ("high impact polystyrene"), which are frequently used in conjunction with PPE to enhance processing and impact strength. These high impact polystyrenes are generally prepared by the copolymerization of polybutadiene and a styrene monomer.

**[0027]** The amount of styrene resin, when present (i.e., the amount of homopolymer, copolymer, or mixture as described above), is usually 1% by weight to 50% by weight, and preferably, 2% by weight to 30% by weight, based on the weight of the entire composition.

**[0028]** As stated previously, the elastomeric copolymer component of the present invention is a blend of an A-B-A' block copolymer (triblock) and an A-B block copolymer (diblock). In the A-B-A' triblock copolymer structure of this invention, the A and A' are polymerized vinyl aromatic hydrocarbon blocks, and B is an ethylene-alkylene block derived from at least one polymerized conjugated diene. In preferred embodiments, the block copolymers preferably contain between 15% and 50% by weight of vinyl aromatics. The A and A' block each have an average molecular weight, preferably number average molecular weight, in the range of 3,000 to 20,000, and preferably 5,000 to 15,000.

**[0029]** In preferred embodiments of this invention, A and A' are polymers independently derived from the group of monomers consisting of styrene, alphas-methyl styrene, para-methyl styrene, vinyl toluene, vinyl xylene, vinyl naphthalene, chlorostyrene, bromostyrene, dibromostyrene, and combinations thereof. Styrene monomer is the preferred monomer.

**[0030]** Center block B of the block copolymer A-B-A' should be almost completely hydrogenated, i.e., the average unsaturation of the copolymer should be reduced to less than about 20% of its original value. In more preferred embodiments, the average unsaturation will be reduced to less than about 10%, and most preferably, less than about 5% of its original value. Methods for accomplishing the hydrogenation of the B block are known in the art.

**[0031]** The B block component of the triblock copolymer of this invention is an ethylene-alkylene component and may be either linear or branched block component. The B block component is preferably derived from a diene monomer or a hydrogenated diene monomer. Examples of such ethylene-alkylene block components are ethylene-propylene, ethylene-butylene, ethylene-hexene, ethylene-pentene, etc. Preferably, the center block B is derived from at least one conjugated diene such as 1,3-butadiene. In the most preferred embodiments, B is obtained via post-hydrogenation of polybutadiene. The average molecular weight, preferably number average molecular weight, of the B block should be in the range of 25,000 to 150,000, and most preferably, in the range of 30,000 to 100,000.

**[0032]** An especially preferred elastomeric triblock copolymer of this invention comprises blocks of styrene and post-hydrogenated polybutadiene within the above-prescribed molecular weight ranges, and is often referred to as "SEBS". Commercial examples of a suitable material are the linear KRATON® G-1650 or 1652 thermoplastic rubbers, available from Shell Chemical Company.

**[0033]** The other part of the blend of elastomeric block copolymers of the invention is an elastomeric diblock copolymer having the structure A-B wherein A is a polymerized vinyl aromatic hydrocarbon block having an average molecular weight, preferably number average molecular weight, of 3,000 to 45,000, and preferably 5000 to 35,000. The B block component of the elastomeric diblock copolymer is an ethylene-alkylene copolymer having an average molecular weight, preferably number average molecular weight, of 25,000 to 150,000, and preferably 30,000 to 100,000. The alkylene portion of the ethylene-alkylene component of the diblock is either linear or branched block component and is preferably derived from a diene monomer or a hydrogenated diene monomer. Examples of such diblock copol-

ymers are ethylene-propylene, ethylene-butylene, ethylene-hexene, ethylene-pentene, etc.

**[0034]** The elastomeric block copolymer blend of this invention comprises in admixture from 75 to 25 weight percent of the triblock component of the blend, and preferably 70 to 30 weight percent thereof. The diblock elastomeric component of the blend comprises, correspondingly, 25 to 75 weight percent of the diblock component of the blend, and preferably 30 weight percent to 70 weight percent thereof.

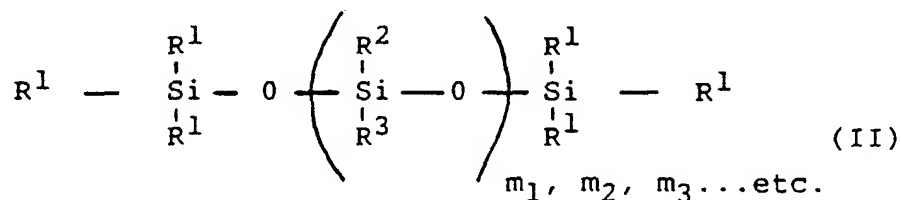
**[0035]** The level of the elastomeric block copolymer blend present in the composition of this invention depends on a variety of factors, such as the particular type of PPE resin used, the contemplated end use of the product, the level of tensile elongation required in such a product, and the presence or absence of other additives in the composition. In preferred embodiments, the composition of this invention comprises in admixture the polyphenylene ether resin and the elastomeric block copolymer blend which is present at a level in the range of 10% by weight to 50% by weight, based on the weight of the total weight of PPE and elastomeric blend composition. In more preferred embodiments, the level is 15% by weight to 40% by weight, while in most preferred embodiments, the level is 20% by weight to 30% by weight, again based on the total weight of PPE and elastomeric blend composition.

**[0036]** The preparation of elastomeric block copolymers, i.e., the triblock or diblock copolymers, of the type used in the present invention is known in the art. For example, one technique involves the successive polymerization of the monomers in solution in the presence of a monolithium hydrocarbon initiator. Further aspects of the preparation of these polymers can be found in EP-A-0 095,098; in U.S.-A- 3,113,986; US-A-3,431,323 ; US-A-3,700,633; and US-A-4,167,507, in EP-A-0 417 510 DE-B-1,222,260; DE-A-2,013,263.

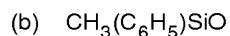
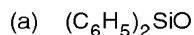
**[0037]** Further, within the scope of this invention, polyorganosiloxanes can also be employed herein. Polyorganosiloxanes are a well known class of synthetic polymers which may be prepared by methods such as, for example, those described in the U.S.-A-2,469,888; US-A-2,469,890; and US-A-3,737,479. The polyorganosiloxanes employed as ingredients in the compositions of the present invention are commonly referred to as "phenylsiloxane fluids".

**[0038]** The phenylsiloxane fluids can have a weight average molecular weight ( $M_w$ ) of up to 100,000 and preferably 800 to 5,000. These fluids can be blended with polyphenylene ether to make the blends of the present invention. These phenylsiloxanes are well known materials and are shown in the Encyclopedia of Polymer Science and Engineering, Vol. 15, pages 258-264, John Wiley and Sons, New York (1989). For example, the phenylsiloxane fluids of the present invention can be made by initially equilibrating dimethyl silicone stock (hydrolysate or distilled cyclic compounds) and a source of chain terminator, such as a trimethylsiloxy unit. Siloxy units having phenyl substituents can be introduced as diphenylsiloxane or methylphenylsiloxane. In most instances, the equilibrated fluid is devolatilized by heat and vacuum after catalyst deactivation. Phenyl substitution, for example, methylphenylsiloxy units which are equilibrated into the dimethylsiloxane backbone, has been found to increase the thermal and oxidative stability of the resulting polydiorganosiloxane. Copolymers of dimethylsiloxane with some methylphenylsiloxane have been found to have lower pour points because the bulky groups interfere with crystallization of the methyl polymer.

**[0039]** In general then, the phenylsiloxane fluids employed as ingredients in the compositions of the invention comprise those of the formula.



wherein each  $\text{R}^1$  is alkyl, haloalkyl, aryl, aralkyl, alkaryl, alkoxy, aryloxy, and halogenated derivatives of the aforesaid aryl, aralkyl, alkaryl, alkoxy, or aryloxy groups, each  $\text{R}^2$  and  $\text{R}^3$  are methyl, phenyl, or phenylethyl, and  $\text{m}_1$ ,  $\text{m}_2$ ,  $\text{m}_3 \dots$  etc. are integers for various combinations of  $\text{R}^2$  and  $\text{R}^3$  such that the polysiloxane is a fluid at room temperature, and preferably wherein they are chemically combined units of the formulae:



and



where there is present in the phenylsiloxane fluid from 20 to 40 mole percentage of (a), or 40 to 80 mole percentage of (b), and 21 to 79 mole percentage of the sum of (a) + (b), based on the total moles of (a), (b), and (c).

**[0040]** The compositions according to the present invention include a polyolefin resin, such as those described in the above-mentioned US-A- 5 166 264. Examples of suitable polyolefins are polyethylene, polypropylene, polyisobutylene, copolymers of ethylene and propylene, copolymers of ethylene and organic esters such as ethylene vinyl acetate, ethylene ethyl acrylate, ethylene methyl acrylate, and the like, as well as mixtures of any polyolefins. The materials themselves are known in the art, as are methods for making them.

**[0041]** Preferred polyolefins are polyethylene, polypropylene, and polybutylene. Especially preferred are low density polyethylene (LDPE), very low density polyethylene, linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), high impact (copolymer) polypropylene, or combinations of any of the above.

**[0042]** The polyolefin is present in an amount of 1% by weight to 30% by weight, based on the weight of the entire composition. A preferred level is 1% by weight to 20% by weight, and a most preferred level is 1% by weight to 15% by weight.

**[0043]** The compositions of the present invention also include a flame retardant plasticizer which is a phosphate compound. Arylphosphates, alkylated arylphosphates, and mixtures of any of these phosphates are often preferred.

**[0044]** Examples of suitable organic phosphates include phenyl bisdodecyl phosphate, ethyldiphenyl phosphate, tri-(nonylphenyl)phosphate, tricresyl phosphate, triphenyl phosphate, alkylated derivatives of triphenyl phosphate, dibutylphenyl phosphate, 2-ethylhexyldiphenyl phosphate, as well as mixtures of any of these materials. Also possible and sometime's preferred for use are di and poly phosphate compounds, such as those described in GB-A- 2,043,083 of William Haaf et al. Examples of these materials are bis diphenyl phosphates of resorcinol or hydroquinone, as well as mixtures which comprise such phosphates. Other suitable phosphates are taught in U.S. -A-4,900,769 of V. Abolins et al. Triarylphosphates in admixture with alkylated aryl phosphates are often preferred. However, a most preferred phosphate is resorcinol diphosphate.

**[0045]** Preferably, the flame retardant phosphate plasticizer is present at a level of from 1% to 25% by weight, based on the weight of the entire composition, and more preferred at a level in the range of 5% by weight to 15% by weight.

**[0046]** Some embodiments of this invention also include one or more phosphite compounds, which often increase the tensile elongation of materials made from these compositions, as well as acting as stabilizers for the present invention.

**[0047]** The phosphite compound used in the present invention can be of various types, such as alkyl phosphites, aryl phosphites, alkyl-aryl phosphites, diphosphites, polyphosphites, and thiophosphites. Many are disclosed in U.S. Patents 4,659,760 and 4,472,546, incorporated herein by reference. Examples of suitable phosphites are triphenyl phosphite, diphenyl phosphite, trimesityl phosphite, dimesityl-phenyl phosphite, trineopentyl phosphite, didecylphenyl phosphite, dichloroethyl phosphite, tributyl phosphite, trilauryl phosphite, tris(nonylphenyl) phosphite, tridecyl phosphite, diphenyldecyl phosphite, tricresyl phosphite, triisooctyl phosphite, tri-2-ethylhexyl phosphite, trioctadecyl phosphite, thiophosphite, phenyldiethyl phosphite, phenyl-di-(2-ethylhexyl) phosphite, isooctyldiphenyl phosphite, diisooctylmonophenyl phosphite, distearyl pentaerythritol diphosphite, bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (commercially available as ULTRANOX® 626 or ULTRANOX® 624), diphenyl isooctyl phosphite, diisooctyl phosphite, distearyl phosphite, diphenylisodecyl phosphite, diisodecyl pentaerythritol diphosphite, poly(dipropylene glycol) phenyl phosphite, and trilauryl trithiophosphite, as well as mixtures of the above.

**[0048]** An effective amount of the phosphite compound is usually in the range of 0.01% by weight to 10% by weight, based on the weight of the entire composition, with 0.1% by weight to 1% by weight being most preferred. The most appropriate range can be determined according to various factors, such as the contemplated end use for the product, as well as the particular identity of the other components present.

**[0049]** Various other additives may be included in the compositions of this invention, their utility being, of course, dependent in part on the contemplated end use for the compositions. Non-limiting examples of these additives include reinforcing agents or fillers such as fibrous glass, graphite whiskers, titanium dioxide, silica, glass fiber, silicon carbide whiskers, carbon fibers, clay, talc, mica and the calcium carbonate; antioxidants; mold release agents; pigments; dyes; heat stabilizers; light stabilizers; processing stabilizers; abrasion resistance compounds; and the like, as well as additional flame retardants and/or plasticizers. These additives are usually included in effective amounts of between 1% and 50% by weight of the total composition.

**[0050]** The compositions of the invention may be prepared by conventional blending techniques such as by melt-blending the ingredients. In a preferred process, some of the ingredients are combined separately as pre-mix blends and then melt blended and extruded from a single or twin screw extruder. For example, blends of polyphenylene ether and the phenylsiloxane fluids can be made by roller mixing or stirring the ingredients and thereafter melt extruding the

pre-blend with the elastomer and any remaining, optional ingredients to obtain a processable blend. Compression molding of the ingredients also can be used.

**[0051]** In another preferred process, the ingredients, including optional ingredients, are first preblended together. The preblended composition is then melt extruded from a single or twin screw extruder. The extrudate may then be cooled (water quench for example) and then pelletized.

**[0052]** Another embodiment of this invention includes an improved electrical conductor article, having a coating material comprising the components described above. For example, an electrical conductor composition comprising in admixture (1) 90% to 50% by weight, preferably 85% to 70% by weight of a polyphenylene ether resin, (2) 10% to 50% by weight, preferably 15% to 30% by weight, of an elastomeric block copolymer comprising a blend of 65% by weight of a styrene-(ethylene-butylene)-styrene triblock copolymer and, correspondingly, 35% by weight of a styrene-(ethylene-butylene) diblock copolymer, wherein the percent by weight of the polyphenylene ether resin and elastomeric block copolymer blend is based on the total weight of PPE resin and elastomer copolymer blend, (3) from 1% by weight to 25% by weight of a flame retardant plasticizer, (4) from 0.01% by weight to 10% by weight of a phosphite, and (5) from 1% by weight to 30% by weight of a polyolefin. More particularly, in the above electrical composition, the flame retardant is resorcinol diphosphate; the phosphite is bis(2,4-di-5-butyl-phenyl) pentaerythritol diphosphite; and the polyolefin is a linear low density polyethylene (LLDPE). Unless otherwise stated, all percent by weights are based on the total weight of the composition.

**[0053]** The coating composition is applied over the surface of an electrical conductor, for example, copper or aluminum wire or cable. (Sometimes, the conductor is first coated with another material, e.g., a material which inhibits or prevents oxidation). Known methods of application are suitable, such as extrusion, followed by cooling. The coating thus forms an excellent electric-insulator for the metal. If desirable, one or more outer or "jacket" layers may be formed over the coating. These layers are also often formed of a polymeric material, such as polyvinyl chloride, a polyester like polybutylene terephthalate, or a polyamide, and can also be applied by extrusion techniques, such as tandem extrusion.

**[0054]** Alternatively, the coating composition of this invention may be used itself as a jacket layer applied over a wire insulating material such as polyvinyl chloride.

**[0055]** Furthermore, the improved compositions described herein are not limited for use as a coating material. They may be used to form any type of formed (e.g., molded [injection or compression molding], calendered, or extruded) article where excellent tensile elongation and/or flame retardance are desirable, as well as flexibility.

**[0056]** The following examples are provided to illustrate various embodiments of this invention.

#### EXAMPLES 1-11

**[0057]** The materials employed in the Examples as component parts were as follows:

**[0058]** Polyphenylene ether (PPE) - Poly(2,6-dimethyl-1,4-phenylene) ether, having an intrinsic viscosity of 0.46 deciliters per gram (dl/g), as measured in chloroform at 25°C.

**[0059]** KRATON® G- 1652 (KG-1652) - Linear styrene(ethylene-butylene)-styrene triblock rubber copolymer, available from Shell Chemical Company, having a total average molecular weight of about 50,400, with each styrene block having an average molecular weight of about 7,700, and the ethylene-butylene block having an average molecular weight of about 35,000.

**[0060]** KRATON® G- 1657 (KG-1657) - Mixture of linear styrene-(ethylene-butylene)-styrene triblock copolymer and a styrene-(ethylene-butylene) diblock copolymer in the ratio of 65/35, with the ratio of total polystyrene to total rubber being 14/86, wherein each styrene block is about 5,000 average molecular weight, and each ethylene-butylene block is about 70,000 average molecular weight.

**[0061]** KRATON® G- 1726 (KG-1726) - Same as KRATON® G-1657, except that the mixture is a 30/70 ratio of triblock to diblock and the total polystyrene to total rubber ratio is 29/71. Each styrene block is about 7,700 average molecular weight and rubber block is about 30,000 average molecular weight.

**[0062]** Plasticizer (71-B) - Mixture of tri(aryl) phosphate and alkylated derivatives thereof as described in U.S.-A-4,945,018.

**[0063]** Plasticizer (RDP) - Resorcinol diphosphate.

**[0064]** Polyolefin PE (GR-8320) - A 20 melt index polyethylene resin.

**[0065]** Siloxane Fluid (SF-1265) - A silicone (polyphenylsiloxane linear fluid; General Electric Company) comprised of a combination of diphenyl and dimethyl siloxane units in a molar ratio of circa 40:60. The fluid typically has a 400 to 600 centistoke viscosity, a  $M_w$  of about 1,600, a  $M_n$  of about 400 and trimethylsiloxy termination.

**[0066]** Phosphite (ULTRANOX U-626) bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (GE Specialty Chemicals, Inc.).

**[0067]** Where reported, the following physical test procedures were carried out:

**[0068]** Tensile Properties: The tensile elongation tests were run at 50.8 cm (20 inches) per minute on test parts cut

from extruded film.

**[0069]** In each Example, as reported in the table below, the component parts were first dry blended for about 30 seconds in a laboratory blender. Each blend was separately extruded in a Werner-Pfleiderer 30 mm twin screw extruder. The melt-blended extrudate of each Example was quenched in water at room temperature and then pelletized.

**[0070]** The pellets of each Example so prepared were then extruded through a die orifice at various temperatures, as set forth in the below table, into a thin films of 0.25 mm (10 mils) in thickness. The films extruded at the various temperatures for each Example were then cut into test specimens having a "dog bone" configuration of about 12.7 cm (5 inches) long for testing for tensile yield (TY), tensile strength (TS) and tensile elongation (TE), employing an Instron Tensile Tester. .

**[0071]** The results, along with the formulation for each Example, and extrusion temperatures are as set forth in the following table.



Ingredients	EXAMPLES										
	1*	2	3*	4*	5*	6	7*	8	9	10	11
PPE	51	51	51	51	51	51	51	51	51	51	51
Triblock/Diblock	242	242		322		242		(83/17)	(65/35)	(48/52)	(30/70)
Triblock	241		321		241		241				
PE (GR-8320)	8	8			8	8	8	8	8	8	8
Phosphite U626	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
71B	17	17	17	17							
RDP					17	17	17	17	17	17	17
Film @ 270°C											
MPa						13.1					
TY (KPSI) 5						(1.9)					
MPa	29.7	15.2	31.7	18.6	38.0	13.1	18.6	18.6	32.4	19.3	17.9
TS (KPSI)	(4.3)	(2.2)	(4.6)	(2.7)	(5.5)	(1.9)	(5.5)	(5.5)	(4.7)	(2.8)	(2.6)
TE (% elongation)	231	269	96	324	170	197	175	174	154	90	58
Film @ 230°C											
TY (KPSI)											
MPa	40.7	21.4									
TS (KPSI)	(5.9)	(3.1)									
TE (% elongation)	91	154									

1. KRATON® G-1652
2. KRATON® G-1657
3. Blend of KRATON® G-1652 and KRATON® G-1726 - ratio of triblock to diblock as shown in each Example 8-11 in ( )
4. KRATON® G-1726
5. KPSI - kilo pounds per square inch

\* Examples 1, 3, 4, 5 and 7 are comparative

[0072] As can be seen from the Examples, when employing the blend of elastomeric multiblock copolymers, namely the blend or triblock and diblock copolymers, significantly better flexibility and elongation are obtained, as compared to Examples using only the triblock copolymer. Please note Examples 2, 4, 6, 8, 9, 10, and 11 compared against comparison Examples 1, 3, 5, and 7. In each case, improved flexibility was obtained with the compositions of this

invention, as demonstrated by tensile strength (TS) and tensile elongation (TE) values.

[0073] Also, when using resorcinol diphosphate (RDP) in place of the 71B, good results were still obtained. The use of RDP significantly reduces fuming and odor when used in place of 71B as a flame retardant.

## Claims

1. A flexible thermoplastic resin composition comprising in admixture a polyphenylene ether resin, from 10% by weight to 50% by weight of an elastomeric block copolymer based on the total weight of polyphenylene ether resin and elastomeric block copolymer, from 1 to 30% by weight of a polyolefin based on the total weight of the composition, and from 1 to 25% by weight of a flame retardant plasticizer based on the total weight of the composition, said flame retardant plasticizer being a phosphate compound characterized in that the elastomeric block copolymer comprises in admixture from 75% by weight to 25% by weight of a triblock copolymer having a hydrogenated structure of A-B-A' and correspondingly from 25% by weight to 75% by weight of a diblock copolymer having a hydrogenated structure of A-B, wherein A and A' are independently selected from polymerized vinyl aromatic hydrocarbon blocks and B is independently selected from an ethylene-alkylene block.
2. The composition of claim 1 wherein A and A' are independently selected from polymerized vinyl aromatic hydrocarbon blocks of 3,000 to 20,000 average molecular weight.
3. The composition of claim 1 wherein B is independently selected from an ethylene-alkylene hydrogenated block copolymer of 25,000 to 150,000 average molecular weight.
4. The composition of claim 3 wherein the ethylene-alkylene block copolymer is independently selected from the group consisting of linear and branched ethylene-alkylene block copolymer.
5. The composition of claim 4 wherein the block copolymer B is ethylene-butylene having an average molecular weight of 30,000 to 100,000.
6. The composition of any preceding claim comprising, in addition to the polyphenylene ether resin and elastomeric block copolymer, a phenylsiloxane fluid having a weight average molecular weight of 800 to 100,000.
7. The composition of claim 6 wherein the phenyl siloxane fluid has a weight average molecular weight of from 800 to 5,000.
8. The composition of claim 1 wherein the elastomeric block copolymer consists essentially of in admixture 65% by weight of a styrene-(ethylene-butylene)-styrene triblock copolymer and, correspondingly, 35% by weight of a styrene-(ethylene-butylene) diblock copolymer said percentage by weight being based on the weight of the elastomeric blend, and further comprises from 0.01% to 10% by weight of a phosphite based on the total weight of the thermoplastic resin composition.
9. The composition of any preceding claim wherein the flame retardant plasticiser is resorcinol diphosphate.
10. The composition of claim 8 wherein the phosphite is a bis (2,4-di-t-butylphenyl)pentaerythritol diphosphite.
11. The composition of any preceding claim wherein the polyolefin is a linear low density polyethylene.
12. The composition of any preceding claim wherein the triblock copolymer component is a styrene-(ethylenebutylene)-styrene copolymer having an average molecular weight of 80,000, and the diblock component is a styrene-(ethylene-butylene) block copolymer having an average molecular weight of 75,000.
13. A process for preparing the thermoplastic resin composition of claim 1 comprising preblending the component parts thereof, feeding the preblend to an extruder wherein the component parts are melt-blended, extruding the melt-blended composition through a die orifice, cooling the extrudate and then pelletizing the extrudate.
14. An electrical conductive article comprising an electrical conductor having a coating thereon wherein said coating comprises the composition of any one of claims 1 to 12.

15. The electrical conductive article of claim 14 wherein the coating covers an insulating layer covering the electrical conductor surface.

16. A formed article wherein the composition of the formed molded article comprises the composition of any one of claims 1 to 12.

## Patentansprüche

1. Eine flexible thermoplastische Harzzusammensetzung aufweisend in Mischung ein Polyphenylenetherharz, von 10 Gew.-% bis 50 Gew.-% eines elastomeren Blockcopolymeren bezogen auf das Gesamtgewichts des Polyphenylenetherharzes und elastomeren Blockcopolymeren, von 1 bis 30 Gew.-% eines Polyolefins bezogen auf das gesamte Gewicht der Zusammensetzung, und von 1 bis 25 Gew.-% eines flammhemmenden Plastifizierungsmittels bezogen auf das Gesamtgewicht der Zusammensetzung, wobei das flammhemmende Plastifizierungsmittel eine Phosphatverbindung ist, dadurch gekennzeichnet, daß das elastomere Blockcopolymer in Mischung von 75 Gew.-% bis 25 Gew.-% eines Triblockcopolymeren aufweist, das eine hydrierte A-B-A'-Struktur hat und entsprechend von 25 Gew.-% bis 75 Gew.-% eines Diblockcopolymeren, das eine hydrierte A-B-Struktur hat, wobei A und A' unabhängig voneinander ausgewählt sind aus polymerisierten vinylaromatischen Kohlenwasserstoffblöcken und B unabhängig ausgewählt ist aus Ethylen-Alkylen-Blöcken.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß A und A' unabhängig ausgewählt sind aus polymerisierten vinylaromatischen Kohlenwasserstoffblöcken mit mittlerem Molekulargewicht von 3000 bis 20 000.

3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß B unabhängig ausgewählt ist aus hydrierten Ethylen-Alkylen Blockcopolymeren mit mittlerem Molekulargewicht von 25 000 bis 150 000.

4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß das Ethylen-Alkylen-Blockcopolymer unabhängig ausgewählt ist aus der Gruppe bestehend aus linearen und verzweigten Ethylen-Alkylen-Blockcopolymeren.

5. Zusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß das Blockcopolymer B ein Ethylen-Butylen ist, das ein mittleres Molekulargewicht von 30 000 bis 100 000 hat.

6. Zusammensetzung nach einem beliebigen der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie zusätzlich zum Polyphenylenetherharz und elastomeren Blockcopolymer ein flüssiges Phenylsiloxan aufweist, das ein Gewichtsmittel des Molekulargewichts von 800 bis 100 000 hat.

7. Zusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß das flüssige Phenylsiloxan ein Gewichtsmittel des Molekulargewichts von 800 bis 5000 hat.

8. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das elastomere Blockcopolymer im wesentlichen aus einer Mischung von 65 Gew.-% eines Styrol-(Ethylen-Butylen)-Styroltriblockcopolymeren und, entsprechend, 35 Gew.-% eines Styrol-(Ethylen-Butylen) Diblockcopolymeren, wobei die Gewichtsprozentangaben auf das Gewicht des elastomeren Blends bezogen sind, und es weiter aufweist zwischen 0,01 bis 10 Gew.-% eines Phosphits bezogen auf das Gesamtgewicht der thermoplastischen Harzzusammensetzung.

9. Zusammensetzung nach einem beliebigen der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das flammhemmende Plastifizierungsmittel Resorcinoldiphosphat ist.

10. Zusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß das Phosphit ein Bis-(2,4-di-t-butylphenyl) pentaerythritoldiphosphit ist.

11. Zusammensetzung nach einem beliebigen der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polyolefin ein lineares Polyethylen niedriger Dichte ist.

12. Zusammensetzung nach einem beliebigen der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Triblockcopolymerbestandteil ein Styrol(Ethylen-Butylen)-Styrolcopolymer ist, das ein mittleres Molekulargewicht von 80 000 hat, und daß der Diblockbestandteil ein Styrol-(Ethylen-Butylen) Blockcopolymer ist, das ein mittleres

Molekulargewicht von 75 000 hat.

13. Verfahren zur Herstellung der thermoplastischen Harzzusammensetzung aus Anspruch 1, bei welchem man die Anteile der Komponenten vormischt, die Vormischung einem Extruder zuführt, wobei die Anteile der Komponenten in der Schmelze gemischt werden, die in der Schmelze gemischte Zusammensetzung durch eine Düsenaustrittsöffnung extrudiert, das Extrudat kühlt und dann das Extrudat pelletisiert.
14. Ein elektrische leitfähiger Gegenstand aufweisend einen elektrischen Leiter, der eine Beschichtung hat, wobei die Beschichtung die Zusammensetzung nach einem beliebigen der Ansprüche 1 bis 12 aufweist.
15. Elektrisch leitfähiger Gegenstand nach Anspruch 14, dadurch gekennzeichnet, daß die Beschichtung eine Isolierungsschicht bedeckt, welche die Oberfläche des elektrischen Leiters bedeckt.
16. Geformter Gegenstand, dadurch gekennzeichnet, daß die Zusammensetzung des geformten Gegenstandes die Zusammensetzung nach einem beliebigen der Ansprüche 1 bis 12 aufweist.

## Revendications

1. Composition thermoplastique souple à base de résine, comprenant en mélange une résine de poly(oxyde de phénylène), 10 % à 50 % en poids d'un copolymère séquencé élastomère par rapport au poids total de résine de poly(oxyde de phénylène) et de copolymère séquencé élastomère, 1 à 30 % en poids d'une polyoléfine par rapport au poids total de la composition et 1 à 25 % en poids d'un plastifiant retardant l'inflammation, par rapport au poids total de la composition, ledit plastifiant retardant l'inflammation étant un phosphate, **caractérisée** en ce que le copolymère séquencé élastomère contient en mélange 75 % en poids à 25 % en poids d'un copolymère tribloc ayant une structure A-B-A' hydrogénée et corrélativement 25 % en poids à 75 % en poids d'un copolymère dibloc ayant une structure A-B hydrogénée, A et A' étant choisis indépendamment parmi des blocs d'hydrocarbure viny-laromatique polymérisé et B étant choisi indépendamment parmi des blocs éthylène-alkylène.
2. Composition selon la revendication 1, pour laquelle A et A' sont choisis indépendamment parmi des blocs d'hydrocarbure viny-laromatique polymérisé, ayant une masse moléculaire moyenne de 3.000 à 20.000.
3. Composition selon la revendication 1, pour laquelle B est choisi indépendamment parmi les copolymères à blocs éthylène-alkylène, hydrogénés, ayant une masse moléculaire moyenne de 25.000 à 150.000.
4. Composition selon la revendication 3, pour laquelle le copolymère à blocs éthylène-alkylène est choisi indépendamment dans le groupe constitué des copolymères à blocs éthylène-alkylène linéaires et des copolymères à blocs éthylène-alkylène ramifiés.
5. Composition selon la revendication 4, pour laquelle le copolymère à blocs B est un copolymère éthylène-butylène ayant une masse moléculaire moyenne de 30.000 à 100.000.
6. Composition selon l'une quelconque des revendications précédentes, qui contient, en plus de la résine de poly(oxyde de phénylène) et du copolymère séquencé élastomère, un phénylsiloxane liquide ayant une masse moléculaire moyenne en poids de 800 à 100.000.
7. Composition selon la revendication 6, dans laquelle le phénylsiloxane liquide est un phénylsiloxane ayant une masse moléculaire moyenne en poids de 800 à 5.000.
8. Composition selon la revendication 1, dans laquelle le copolymère séquencé élastomère est constitué essentiellement d'un mélange de 65 % en poids d'un copolymère tribloc styrène-(éthylène-butylène)-styrène et corrélativement 35 % en poids d'un copolymère dibloc styrène-(éthylène-butylène), lesdits pourcentages en poids étant basés sur le poids du mélange élastomère, et qui contient en outre 0,01 % à 10 % en poids d'un phosphite par rapport au poids total de la composition thermoplastique à base de résine.
9. Composition selon l'une quelconque des revendications précédentes, dans laquelle le plastifiant retardant l'inflammation est le diphosphate de résorcinol.

10. Composition selon la revendication 8, dans laquelle le phosphite est le diphosphite de bis(2,4-di-t-butylphényle) et de pentaérythritol.

11. Composition selon l'une quelconque des revendications précédentes, dans laquelle la polyoléfine est un polyéthylène linéaire basse densité.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle le constituant copolymère tribloc est un copolymère styrène-(éthylène-butylène)-styrène ayant une masse moléculaire moyenne de 80.000 et le constituant dibloc est un copolymère à blocs styrène-(éthylène-butylène) ayant une masse moléculaire moyenne de 75.000.

13. Procédé de préparation de la composition thermoplastique à base de résine selon la revendication 1, qui comprend les étapes consistant à mélanger au préalable les parties constitutantes de la composition, à introduire le prémélange dans une extrudeuse où les parties constitutantes sont mélangées à l'état fondu, à extruder par l'orifice d'une filière la composition mélangée à l'état fondu, à refroidir le produit extrudé et à mettre ensuite le produit extrudé sous la forme de pastilles.

14. Article conducteur de l'électricité, comprenant un conducteur électrique portant un revêtement, pour lequel ledit revêtement comprend la composition selon l'une quelconque des revendications 1 à 12.

15. Article conducteur de l'électricité selon la revendication 14, dans lequel le revêtement recouvre une couche isolante couvrant la surface du conducteur électrique.

16. Article façonné pour lequel la composition de l'article moulé façonné comprend la composition selon l'une quelconque des revendications 1 à 12.